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Steam and dry reforming of methane on Rh: Microkinetic analysis and hierarchy of kinetic models

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ABSTRACT

CH_4 steam reforming (SR) and dry reforming (DR) on Rh have been analyzed using a comprehensive, thermodynamically consistent microkinetic model. Our analysis pointed out mechanistic analogies between the two processes. In particular, regardless of the co-reactant, methane consumption proceeds via pyrolysis and carbon oxidation by OH* ($CH_4 \rightarrow C^* \rightarrow CO^*$), and the role of the co-reactant (either CO_2 or H_2O) is to provide the main oxidizer, OH*. Moreover, in line with isotopic kinetic experiments reported in the literature, methane activation is predicted to be the rate-determining step, and all of the steps involving co-reactant turn out to be quasi-equilibrated. It also was found that under typical experimental conditions, SR and DR always occur with water–gas shift (WGS) reaction close to equilibrium. Adopting a systematic reduction methodology, we propose a hierarchy of models for SR and DR. In particular, first a reduced microkinetic model and then overall rate equations for the SR, DR, and WGS reactions are derived from the microkinetic models. Overall, our kinetic analysis is able to predict correctly the most important features found in experiments, namely that the overall reaction rate exhibits a first-order dependence on CH_4 concentration and is independent of the co-reactant (H_2O or CO_2). Product inhibition, which becomes important at lower temperatures, also is predicted.

1. Introduction

The possibility of a hydrogen economy [1,2] and the need for alternative clean fuels have renewed interest in hydrogen and especially in novel routes and/or sources for delocalized hydrogen production [3,4] as an alternative to the conventional steam reforming (SR) on Ni catalysts. The latter is an energy-intensive process (almost half of natural gas is burnt to supply the necessary heat), conducted at high pressure (15–30 atm) and characterized by a long residence time (1 s) [5]. Consequently, steam reformers on Ni are too bulky for use in decentralized, small-scale H_2 production [6] and must be replaced with processes that can occur at short contact times. Rh is a very good catalyst for CH_4 SR, dry reforming (DR), and partial oxidation (POX) of methane with excellent conversion and selectivity to syngas at very short contact times [7–9]; that is, the conventional bulky reformers could be replaced by about 100- to 1000-fold smaller reactors running on Rh. This attribute makes SR, DR, and POX on Rh possible solutions for distributed production of H_2 from natural gas.

Modeling of reforming reactors on Rh requires, among other things, reliable kinetic models, validated in an operating range relevant to practical applications. Understanding of the catalytic process at a fundamental level aids optimization of the process and the catalysts. In this respect, a comprehensive microkinetic model is an important tool for consolidating fundamental information about a catalytic process under different operating conditions [10,11]. Different from the semiempirical approaches, microkinetic modeling not only affords an analysis of the performance of catalytic reactors—in principle, valid over a wide range of operating conditions—but also offers fundamental insights into the reaction mechanism, leading, in conjunction with experimental information, to a deeper understanding of the catalytic process. In fact, it can elucidate the predominant paths, the rate-determining step (RDS) and the most abundant reactive intermediates (MARI) without *a priori* assumptions on elementary steps. It is an essential tool when fundamental aspects, such as the possible interaction between the surface and gas-phase chemistry, must be quantified [12]. But its implementation is often a demanding task in terms of CPU time, especially when fast model responses are required (e.g., for online process control and computational fluid dynamics [CFD] simulations) or fundamental information about the catalytic process is not needed. In those cases, overall rate expressions are often preferred. Thus, it is apparent that a hierarchy of kinetic models is called for in reactor modeling [13,14].

Several kinetic models for reforming and partial oxidation of CH_4 on Rh catalysts, both detailed [15–17] and molecular [18–20],

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Table 1
Summary of key experimental findings for SR and DR

Author	Notes	Findings/comments	Proposed kinetic/mechanism
Wei and Iglesia [36]	*Catalyst:* Rh H_2O/CH_4 and CO_2/CH_4: 0.4 to 2 *Temperature*: 873 to 1023 K *Conversions*: lower than 5–10%	a) CH_4 activation is the only kinetically relevant step b) No kinetic effect of co-reactant (either H_2O or CO_2) c) WGS always occurs at equilibrium along with SR/DR d) No product inhibition on reaction rate e) SR and DR proceed with the same rate	a) Methane reacts via pyrolysis: $CH_4 \rightarrow C^* + 4H$ b) Methane pyrolysis is the RDS c) C^* oxidation by O^* d) Co-reactant steps assumed at equilibrium
Rostrup-Nielsen and Hansen [41]	*Catalyst:* Ni, Ru, Rh, Pd, Ir, Pt	a) SR and DR proceed with the same rate b) No kinetic effect of co-reactant (either H_2O or CO_2) c) WGS at equilibrium	a) Methane reacts via pyrolysis: $CH_4 \rightarrow C^* + 4H$ b) C^* oxidation by O^* c) RDS: CH_4 pyrolysis and C^* oxidation
Bradford and Vannice [38]	*Catalyst:* Ni CH_4–CO_2 mixtures *Temperature*: 673 to 823 K	a) CO_2 has a negligible effect on CH_4 conversion at ratios $CO_2/CH_4 \geqslant 1$ b) A negative reaction order in CO_2 for $CO_2/CH_4 \leqslant 1$ c) Reverse-WGS at equilibrium	a) Methane reacts via pyrolysis: $CH_x^* + {}^* \rightarrow CH_{x-1}^* + H^*$ b) CH_x^* reacts with surface OH^* (from reverse WGS) to CH_xO c) CH_4 pyrolysis and CH_xO decomposition to CO are RDS
Donazzi et al. [18,23]	*Catalyst:* Rh H_2O/CH_4 and CO_2/CH_4: 1 to 4 *Temperature*: 300 to 850 K *Conversions*: up to 100%	a) 1st-order dependence on CH_4 b) No kinetic effect of H_2O in SR c) Kinetic effect of CO_2 in DR for $CO_2/CH_4 \leqslant 1$ d) SR and DR proceed with the same rate for co-reactant/$CH_4 > 1$ e) Product inhibition possible	a) DR is considered the summation of SR and reverse WGS b) For $CO_2/CH_4 > 1$, the reverse WGS is at equilibrium

have been reported, but in general they suffer from different limitations, including a limited range of validity or lack of thermodynamic consistency. We have recently proposed [21,22] a new version of the microkinetic model of Mhadeshwar and Vlachos [16], using a comprehensive experimental data set of various processes [18,23], according to a hierarchical multiscale methodology [16,21,22,24,25]. The activation energies are predicted using the unity bond index quadratic exponential potential (UBI-QEP) theory [26,27], and coverage effects are accounted for using DFT. Our single-site, mean field-based microkinetic model is able to predict quantitatively the effect of different feed compositions and temperature for various reacting systems, including SR ($CH_4 + H_2O$), DR ($CH_4 + CO_2$), POX ($CH_4 + O_2$), hydrogen ($H_2 + O_2$) and carbon monoxide ($CO + O_2$)-rich combustion, the water–gas shift (WGS; $CO + H_2O$), and the reverse water–gas shift (RWGS; $CO_2 + H_2$).

In this work, we present a detailed analysis of the catalytic mechanism of SR and DR processes to rationalize the experimental data and trends. Then we derive a hierarchy of models for CH_4–H_2O and CH_4–CO_2 reacting systems, ranging from a reduced microkinetic model to overall two-step rate expressions for SR and DR. In contrast to the classical approaches, where overall expressions are usually based either on *ad hoc* power-law fitting or on an *assumed* reaction mechanism and RDS (e.g., Langmuir–Hinshelwood–Hougen–Watson [28]), we perform a top-down hierarchical model reduction, where the information of the higher-level model is exploited for the development of the lower-level model. In this way, no *a priori* assumptions are required at any step. In particular, the paper comprises two main sections. In the first section, we report a microkinetic analysis of CH_4–H_2O and CH_4–CO_2 reacting systems using the full microkinetic model [21,22]. This analysis involves identification of the main elementary-like reaction paths, MARI and RDS, with no *a priori* assumption on reaction steps. In the second section, we propose a hierarchical chemistry reduction [29–31] of the full microkinetic model to derive a reduced microkinetic model for $CH_4/H_2O/CO_2$ reacting systems and two-step rate expressions. In doing so, the two-step rate expressions are not based on chemical hypotheses, and the effective parameters are not determined by regression of experimental data, but rather are directly related to the rate constants of the elementary-like reactions of the microkinetic model. Comparisons to experimental data and to the key experimental findings reported in the literature also are made. For the sake of clarity, a summary of such literature findings is reported in Table 1.

2. Full microkinetic model-based analysis

For the analysis, we used our C_1 single-site microkinetic model [21,22], under the assumption of thermal equilibrium between the catalyst particle and its environment and the mean-field approximation.

2.1. Comparison to experimental data

The SR and DR data of Donazzi et al. [23] in an annular reactor were simulated using a one-dimensional heterogeneous model [19,32]. This model was assessed in previous work. In addition, transport effects are not significant under most conditions. Model equations and reactor details are reported in Table 2. The measured experimental Rh dispersion and weight (5% and 10 mg of 4% Rh-Al_2O_3, respectively) were considered input in the simulations, giving rise to a Rh surface per unit reactor volume (a_v) of 600 cm^{-1}. Only this parameter should be input each time that the catalyst changes; the kinetic parameters remain the same. Fig. 1 compares predictions using the entire microkinetic model of 82 elementary-like reactions [21,22] to experimental data, in terms of CH_4 conversion. The full microkinetic model was able to predict both SR and DR experimental data reasonably well, except for the DR experiment with $CO_2/CH_4 = 1$, where the model overestimates the CH_4 conversion considerably (square symbols in Fig. 1b). Fig. 2 compares DR and SR at different temperatures (solid lines). The model correctly predicted the trend with temperature for both reactants and products.

2.2. Main reaction paths and rate-determining step

Here we present an analysis of the full microkinetic model for SR and DR on Rh [21,22], with the aim of identifying the main elementary-like reaction pathways, the RDS, and the main molecular stoichiometries. We refer our analysis to the experimental data reported in Fig. 2.

2.2.1. Steam reforming

To identify the main reaction pathways from reactants to products involved in SR, we carried out reaction path analysis (RPA), based on the net production rate of each surface species [33]. The analysis was performed at three selected temperatures (400, 500, and 600 °C), at which moderate to high conversions were observed (Fig. 2). Results are reported in Fig. 3a for 500 °C. Similar results were found for the other two temperatures investigated.